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(71) Applicant *(for all designated States except US)*: MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG[DE/DE]; Frankfurter Strasse 250, D-6100 Darmstadt (DE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : STANFORD, John, Edward [GB/GB]; 1 Queens Road, Parkstone, Poole, Dorset (GB). SAGE, Ian, Charles [GB/GB]; 58 Wentworth Drive, Broadstone, Dorset BH18 8EG (GB). GRIFFITHS, John [GB/GB]; 9 Ashlea Close, Gosforth, Leeds (GB). TAILOR, Suresh [GB/GB]; 68 Glembrook Drive, Bradford BD7 2QF (GB). LEWIS, Martin [GB/GB]; 38 Lyndhurst Gardens, Finchley, London N3 1TD (GB). WILTSHIRE, Michael [GB/GB]; 3 The Brackens, High Wycombe, Bucks HP11 1EV (GB).

(74) Common Representative: MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG; Frankfurter Strasse 250, D-6100 Darmstadt (DE).

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(54) Title: LIQUID CRYSTAL DISPLAY DEVICES AND LIQUID CRYSTAL MEDIUM TO BE USED THEREIN

(57) Abstract

The invention concerns a liquid crystal display device containing a liquid crystalline medium which comprises a host material and at least one fluorescent dye, characterized in that the host material is composed of at least two liquid crystalline compounds, one having a negative or a positive dielectric anistropy, and one having a neutral dielectric anisotropy, further characterized in that the host mixture has an extinction coefficient between 300 and 400 nm of less than 2×10^2 and in that the liquid crystal medium further comprises an efficient amount of an energy transfer agent having an extinction coefficient between 300 and 400 nm of at least 10^4, a solubility in the liquid crystal medium of at least 0.1 % and a fluorescence quantum yield of at least 0.2.

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Liquid crystal display devices and liquid crystal medium to be used therein

The invention refers to a liquid crystal display device containing a liquid crystal medium which comprises a host material and at least one fluorescent dye. Fluorescent liquid crystal display devices of this type are in principle known, e.g. from U.S. patents 4,208,106, 4,211,473 and 4,556,287, from GB patent 21 69 092 and from the publications in Electronic Letters Vol. 22, No. 18, pp. 962-963 of August 28, 1986, and Proceedings Eurodisplay 1987, pp. 149-151.

In these display devices in a nematic and/or cholesteric liquid crystal host material a pleochroic fluorescent dye is dissolved such that by a guest-host interaction the molecules of the pleochroic dye may align with those of the liquid crystal material. As a rule, for these devices especially cyanobiphenyls or other liquid crystal materials containing conjugated aromatic ring systems are employed. These aromatic liquid crystal materials have the advantage that invisible UV light is absorbed by the host and in the presence of a suitable fluorescent dye an energy transfer process can occur during which the dye molecule obtains energy from the excited host and can then emit light in the visible region of the spectrum.

The broad application of such fluorescent display devices fails, however, by the fact that the in principle good display characteristics suffer from a gradual fading of the fluorescent emission, possibly a result of chemical degradation of the dye caused by the incident UV light. It has, therefore, been a task of the present invention to find fluorescent liquid crystal display devices which do not only possess good display characteristics but also an improved stability and a longer lifetime.

This task could be solved by the present invention. Surprisingly it was found that the stability and lifetime of the fluorescent dye is dependent on the nature of the host material and that especially a host having a low extinction coefficient between 300 and 400 nm and being composed both of compounds having a neutral dielectric anisotropy and of compounds having a positive or a negative dielectric anisotropy, possesses especially advantageous properties when it is used in connection with a compound having a high extinction coefficient between 300 and 400 nm and which acts as an energy-transfer agent for the fluorescent dye.

Subject of the present invention is therefore a liquid crystal display device containing a liquid crystalline medium which comprises a host material and at least one fluorescent dye, characterized in that the host material is composed of at least two liquid crystalline compounds, one having a negative or a positive dielectric anisotropy and one having a neutral dielectric anisotropy, further characterized in that the host mixture has an extinction coefficient between 300 and 400 nm of less than 2×10^2 and in that the liquid crystal medium

further comprises an efficient amount of an energy-transfer agent having an extinction coefficient between 300 and 400 nm of at least 10^4, a solubility in the liquid crystal medium of at least 0.1 % and a fluorescence quantum yield of at least 0.2.

A further subject of the present invention is the liquid crystalline medium for use in this display.

The liquid crystal compounds which can be used as the host material are known and the skilled worker can choose an appropriate material according to the principles given above. To fulfill the demand for a low extinction coefficient between 300 and 400 nm at least one of the rings usually present in liquid crystalline compounds must be hydrogenated, preferably fully hydrogenated compounds are used and preferably the extinction coefficient is less than 50.

Examples for the liquid crystalline compounds with a positive dielectric anisotropy are R-Cy-Cy-CN, R-Cy-CH_2-CH_2-Cy-CN and R-Cy-Cy-Cy-CN, Cy in each case being 1,4-cyclohexylene.

Examples for liquid crystalline compounds with a negative dielectric anisotropy are R-Cy-Cy-  (CN being axially oriented) and R-Cy-CH(CN)-CH_2-Cy-R'.

Preferred compounds with neutral dielectricity can be characterized by the formula $R^1-(Cy)_n-Z-Cy-R^2$, wherein R^1 and R^2 are alkyl, alkenyl, alkoxy or alkenyloxy, n is 1 or 2, Z is a single bond, -COO- or $-CH_2-CH_2$ and Cy is 1,4-cyclohexylene or 1,4-cyclohexen-(2)-ylene.

Other suitable liquid crystalline compounds can be taken from "Flüssige Kristalle in Tabellen" (liquid crystals in tables), VEB Deutscher Verlag für Grundstoffindustrie, 2nd edition, 1976 and "Flüssige Kristalle in Tabellen II", ibid, 1st edition (1984).

Compounds with negative or positive dielectric anisotropy are defined as having $|\Delta\varepsilon| > 2.0$, whereas compounds with neutral dielectricity have $\Delta\varepsilon$ in the range from -2.0 to +2.0.

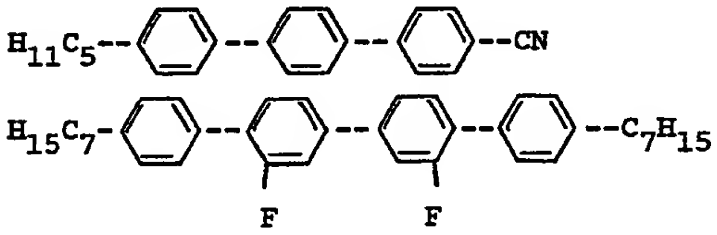
In the host mixture the neutral compound(s) as a rule amount to about 10 to 90 % by weight, mixtures containing about 20 to 70 % being preferred.

Due to the low extinction coefficient in the range from 300 to 400 nm this host mixture is not suited for use in an indirectly excited display. This can be rectified, however, by addition of an effective amount of a suitable material which possesses a high extinction coefficient between 300 and 400 nm and which acts as an energy-transfer agent which transmits the absorbed energy to the fluorescent dye.

As an energy-transfer agent in principle all compounds are suitable which possess an extinction coefficient between 300 and 400 nm of at least 10^4, preferably of at least 15000, which are sufficiently soluble in the liquid crystalline host mixture and which possess an emission

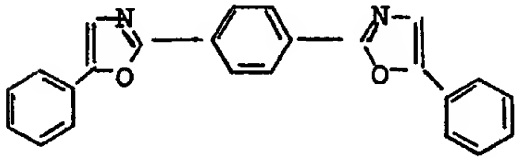
wavelength which overlaps with the excitation wavelength of the fluorophor. The energy-transfer agent thereby allows not only indirect excitation of the fluorophor to be used but surprisingly acts also as UV-absorbing stabilizer leading to further enhancement in photostability of the liquid crystal medium.

Suitable energy-transfer agents possess as a rule a linear aromatic or heteroaromatic structure as it is exemplified by the following compounds:

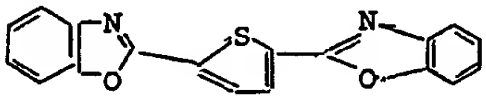


T15 (340 nm)*

DFQP7.7 (340 nm)*



POPOP (394 nm)*



BOXT (394 nm)*

* Excitation maximum

Basically, however, a large variety of compounds is suitable, especially compounds which are known as fluorescent whitening agents. A survey on such compounds is found in Rev. Prog. Coloration Vol. 17 (1987), pp. 39-55 and the references cited therein. From this large number of known compounds the skilled worker can chose

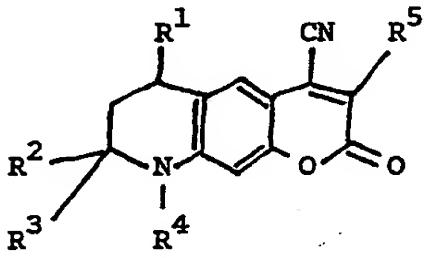
easily suitable compounds according to the above mentioned principles, like e.g. excitation and emission wavelength, solubility and effectivity. Preferably the fluorescence quantum yield in the solution of the liquid crystal medium should be higher than 0.2. Therefore, as a rule, aldehyde and ketone groups which usually lower the quantum yield and which also may cause accelerated photodegradation are not present in preferred structures and it is also preferred that the compounds are as planar as possible to ensure efficient fluorescence.

The energy-transfer agents are used in an effective amount which may vary depending on the nature of the agent but which can be easily optimized by a skilled worker. As a rule amounts of about 0.05 to about 10 weight %, preferably of about 0.1 to about 6 % are used.

The fluorescent dyes, capable of being used in the liquid crystal medium of the present invention, are dyes that exhibit anisotropic absorption and emission, i.e. molecules which have the property that the absorption coefficient and consequently the fluorescence intensity of the dye molecule is strongly dependent on the alignment between the plane of polarization of the incident radiation and the molecular axis of the dye molecule. Basically, these are rigid, lath-shaped fluorescent dyes possessing a uniform major polarization axis which are well known to those skilled in the art.

Examples of fluorescent dyes useful in this invention are usually aromatic compounds such as those named in U.S. patents 4,556,287, 4,211,473 and 4,208,106, GB patent 2,169,092, EP patent 4655 as well as in the references cited in these patents, all of these publi-

cations being incorporated by reference into this application. As a further preferred embodiment of the present invention it has been found that cyano-coumarin-dyes of formula I



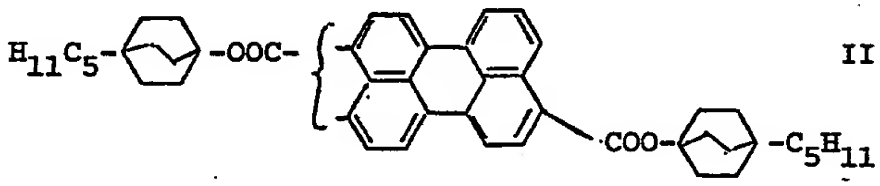
I

are especially well suited for the use in these display devices. Preferred are dyes wherein R^5 is a benzoxazolyl- and especially a 5-chloro-1,3-benzoxazol-2-yl radical.

The emission wavelength of these dyes is in any case in the visible range of the spectrum. Preferred is a wavelength in the range of from 550 to 620 nm. The dyes as a rule are used in concentrations with regard to the complete liquid crystal medium of about 0.05 to about 2 % by weight, concentrations of about 0.1 to about 1 % being preferred.

It is also possible to use different dyes of similar or different structures and emission wavelengths. In some cases it has been found that by the use of a mixed dye system, e.g. a green and a red fluorophor, not only the brightness of the display can be increased but that there is a further gain in photostability. This is therefore a further preferred aspect of this invention.

Among these mixed dye systems with a green and a red dye are especially preferred mixtures containing the green perylene dye of formula II (isomer mixture)



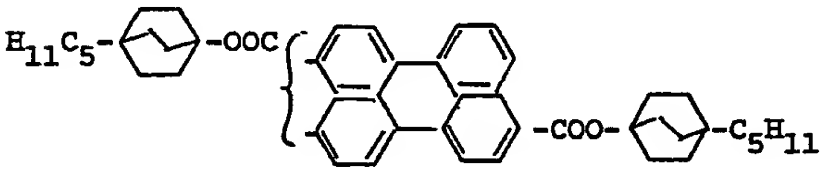
II

and its homologues.

For an additional improvement of the light stability of the inventive liquid crystal medium small amounts of conventional UV stabilizers can be added as they are described in European patent application 19 58 98, British patent application 21 17 390 and the references cited therein. Amounts of about 0.05 to 1 % of these stabilizers are preferred.

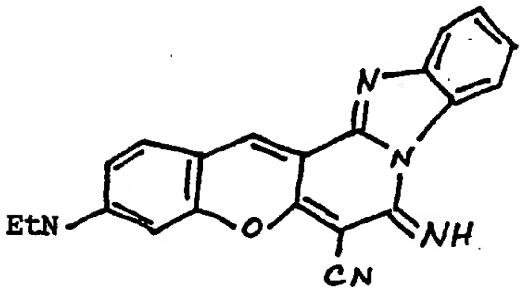
In the examples dyes of the following structures are used:

Dye 1 (a green perylene dye)

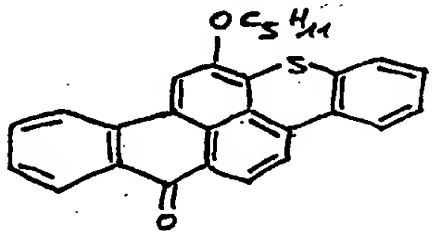


(isomer mixture)

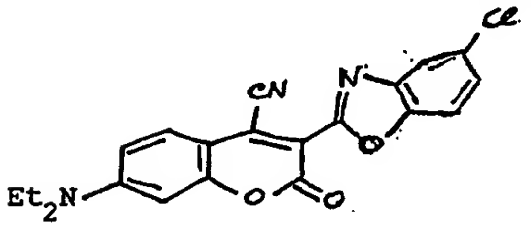
Dye 2 (a red benzopyran dye)



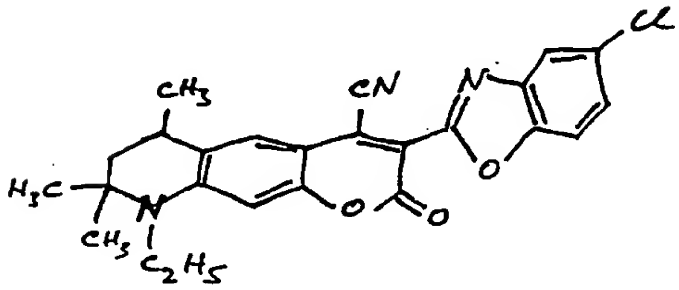
Dye 3 (a red benzanthrone dye)



Dye 4 (a red cyanocoumarin dye)



Dye 5 (a red cyanocoumarin dye)



In the examples as energy-transfer agents are used T15, POPOP, DFQP7.7 and BOXT, the structures of which are given above.

In the examples the following host mixtures are used:

ZLI 2585 composed of:

34 % r-1-cyan-cis-4-(trans-4-butylcyclohexyl)-1-heptyl-cyclohexan
29.1 % r-1-cyan-cis-4-(trans-4-pentylcyclohexyl)-1-pentyl-cyclohexan
10.8 % trans,trans-4-methoxy-4'-propylcyclohexylcyclohexan
9.7 % trans,trans-4-ethoxy-4'-propylcyclohexylcyclohexan
4.8 % trans,trans-4-propylcyclohexyl-cyclohexan-4'-carbonsäure-trans-4-propylcyclohexylester
3.9 % trans,trans-4-propylcyclohexyl-cyclohexan-4'-carbonsäure-trans-4-pentylcyclohexylester
3.9 % trans,trans-4-butylcyclohexyl-cyclohexan-4'-carbonsäure-trans-4-propylcyclohexylester
3.9 % trans,trans-4-butylcyclohexyl-cyclohexan-4'-carbonsäure-trans-4-pentylcyclohexylester

ZLI 5310 composed of:

7 % trans,trans-4-ethylcyclohexylcyclohexan-4'-carbonitril
9 % trans,trans-4-propylcyclohexylcyclohexan-4'-carbonitril
15 % trans,trans-4-butylcyclohexylcyclohexan-4'-carbonitril
9 % trans,trans-4-pentylcyclohexylcyclohexan-4'-carbonitril

11 % trans,trans-4-ethoxy-4'-propylcyclohexylcyclohexan

20 % trans,trans-4-propoxy-4'-propylcyclohexylcyclohexan

15 % trans,trans-4-methoxy-4'-pentylcyclohexylcyclohexan

6 % trans,trans-4-propylcyclohexyl-cyclohexan-4'-carbonsäure-trans-4-pentylcyclohexylester

8 % trans,trans-4-methoxy-4'-propylcyclohexylcyclohexan

ZLI 2359 composed of:

18 % trans,trans-4-ethylcyclohexylcyclohexan-4'-carbonitril

5 % trans,trans-4-propylcyclohexylcyclohexan-4'-carbonitril

15 % trans,trans-4-butylcyclohexylcyclohexan-4'-carbonitril

5 % trans,trans-4-pentylcyclohexylcyclohexan-4'-carbonitril

5 % trans,trans-4-heptylcyclohexylcyclohexan-4'-carbonitril

17 % trans-4-propylcyclohexancarbonsäure-(trans-4-propylcyclohexylester)

18 % trans-4-propylcyclohexancarbonsäure-(trans-4-pentylcyclohexylester)

5 % trans,trans-4-propylcyclohexyl-cyclohexan-4'-carbonsäure-trans-4-pentylcyclohexylester

6 % trans,trans-4-butylcyclohexyl-cyclohexan-4'-carbonsäure-trans-4-propylcyclohexylester

6 % trans,trans-4-butylcyclohexyl-cyclohexan-4'-carbonsäure-trans-4-pentylcyclohexylester

Example 1

A mixture was made containing

Dye 1	0.8 %
ZLI 2585	98.95 %
POPOP	0.25 %

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a green fluorescent display with dark non-emissive segments was obtained.

Example 2

A mixture was made containing

Dye 1	0.8 %
5310	94.2 %
T 15	5.0 %

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a green fluorescent display with dark non-emissive segments was obtained.

Example 3

A mixture was made containing

Dye 1	0.8 %
5310	94.2 %
DFQP 7.7	5.0 %

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a green fluorescent display with dark non-emissive segments was obtained.

Example 4

A mixture was made containing

Dye I	0.8 %
5310	98.2 %
BOXT	1.0 %

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a green fluorescent display with dark non-emissive segments was obtained.

Example 5

A mixture was made containing

Dye 1	0.8 %
ZLI 2359	94.2 %
T 15	5.0 %

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a green fluorescent display with dark non-emissive segments was obtained.

Example 6

A mixture was made containing

Dye 1	0.8 %
ZLI 2359	94.2 %
DFQP 7.7	5.0 %

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a green fluorescent display with dark non-emissive segments was obtained.

Example 7

A mixture was made containing

Dye 1	0.8 %
ZLI 2359	98.2 %
BOXT	1.0 %

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a green fluorescent display with dark non-emissive segments was obtained.

Examples 8-14

Mixtures analogous to examples 1-7 are used containing 0.15 % of Dye 2 instead of Dye 1.

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a red fluorescent display with dark non-emissive segments was obtained.

Examples 15-21

Mixtures analogous to examples 1-7 are used containing 0.20 % of Dye 3 instead of Dye 1.

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a red fluorescent display with dark non-emissive segments was obtained.

Examples 22-28

Mixtures analogous to examples 1-7 are used containing 0.30 % of Dye 4 instead of Dye 1.

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a red fluorescent display with dark non-emissive segments was obtained.

Examples 29-35

Mixtures analogous to examples 1-7 are used containing 0.30 % of Dye 5 instead of Dye 1.

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a red fluorescent display with dark non-emissive segments was obtained.

Examples 36-42

Mixtures analogous to examples 1-7 are used containing 0.15 % of Dye 1 and 0.15 % of Dye 2 instead of Dye 1.

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a orange-red fluorescent display with dark non-emissive segments was obtained.

Examples 43-49

Mixtures analogous to examples 1-7 are used containing 0.20 % of Dye 1 and 0.20 % of Dye 3 instead of Dye 1.

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a orange-red fluorescent display with dark non-emissive segments was obtained.

Examples 50-56

Mixtures analogous to examples 1-7 are used containing 0.30 % of Dye 1 and 0.30 % of Dye 4 instead of Dye 1.

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a orange-red fluorescent display with dark non-emissive segments was obtained.

Examples 57-63

Mixtures analogous to examples 1-7 are used containing 0.30 % of Dye 1 and 0.30 % of Dye 5 instead of Dye 1.

When filled into an electro-optic display cell and excited with a lower power ultra violet lamp a orange-red fluorescent display with dark non-emissive segments was obtained.

Comparative examples

The following liquid crystal media contain each 0.8 % of dye 1. The other components of these media, i.e. the liquid crystal host and the energy-transfer agent (ETA) and its percentage as well as the fluorescent half-life of each of these media are compiled in the following:

Medium No.	Host	ETA	Fluorescent half-life
1	E7	T15 8 %	317 hrs
2	ZLI-1083	POPOP 0.25 %	415 hrs
3	ZLI-1083	DFQP 5 %	408 hrs
4	ZLI-2359	T15 8 %	1368 hrs
5	ZLI-2359	DFQP 5 %	1517 hrs
6	ZLI-2359	BOXT 1 %	1281 hrs

It is clearly apparent from the above data that the media according to the present invention (media 4, 5 and 6) show markedly better life-times than the media 1, 2 and 3, the host of which is based on liquid crystals

having an extinction coefficient between 300 and 400 nm of considerably more than 2 x 10^2. E7 is based on cyanobiphenyls, whereas ZLI-1083 is based on phenylcyclohexanes. The lifetests were carried out by filling a commercially produced polyimide aligned display cell, 7 microns thick, with the medium under test. The cells were exposed to filtered Xenon arc radiation in a Heraeus Sun Test machine, followed by measurement of the fluorescence intensity in a Perkin Elmer LS5 spectrofluorimeter.

Patent Claims

1. Liquid crystal display device containing a liquid crystalline medium which comprises a host material and at least one fluorescent dye, characterized in that the host material is composed of at least two liquid crystalline compounds, one having a negative or a positive dielectric anisotropy, and one having a neutral dielectric anisotropy, further characterized in that the host mixture has an extinction coefficient between 300 and 400 nm of less than 2×10^2 and in that the liquid crystal medium further comprises an efficient amount of an energy transfer agent having an extinction coefficient between 300 and 400 nm of at least 10^4, a solubility in the liquid crystal medium of at least 0.1 % and a fluorescence quantum yield of at least 0.2.

2. Display device according to Claim 1, characterized in that the host material is composed of fully saturated liquid crystal compounds.

3. Display device according to Claim 1 or 2, characterized in that the energy transfer agent comprises at least one compound having a structure element of formula

$$-Ar^1-Ar^2-Ar^3-$$

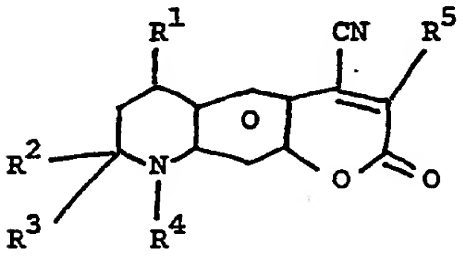
wherein Ar^1, Ar^2 and Ar^3 are identical or different and are selected from the group consisting of unsubstituted 1,4-phenylene, 1,4-phenylene substituted by 1 or 2 fluorine atoms, and heteroaromatic ring structures.

4. Display device according to Claim 3, characterized in that the energy transfer agent comprises at least one anisotropic compound.

5. Display device according to one of Claims 1 to 4, characterized in that the liquid crystalline medium comprises a mixed dye system.

6. Display device according to Claim 5, characterized in that an energy transfer from a green to a red fluorophor is used.

7. Display device according to one of Claims 1 to 6, characterized in that the liquid crystal medium comprises a fluorescent dye of the general formula I

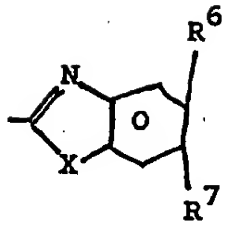


I

wherein

R^1, R^2 and R^3 are each independently alkyl with 1 to 6 carbon atoms

R^4 is alkyl or cycloalkyl with up to 7 carbon atoms possibly substituted once or twice with hydroxy, cyano, alkoxy with 1 to 3 carbon atoms or alkoxycarbonyl with 1 to 3 carbon atoms

R^5 is  or 

R^6 and R^7 is hydrogen, chlorine, bromine, cyano, alkyl, alkoxy, alkoxycarbonyl or carbalkoxy each with up to 7 carbon atoms in the alkyl chain

X is O or N-R^8

R^8 is hydrogen or alkyl with 1 to 3 carbon atoms.

8. Liquid crystal medium containing at least one fluorescent dye and a host material, characterized in that the host material is composed of at least two liquid crystalline compounds, one having a negative or a positive dielectric anisotropy, and one having a neutral dielectric anisotropy, further characterized in that the host mixture has an extinction coefficient between 300 and 400 nm of less than 2×10^2, and in that it further comprises an efficient amount of an energy transfer agent having an extinction coefficient between 300 and 400 nm of at least 10^4, a solubility in the liquid crystal medium of at least 0.1 %, and a fluorescence quantum yield of at least 0.2.

9. Liquid crystal medium according to Claim 8, characterized in that the host material is composed of fully saturated liquid crystal compounds.

10. Liquid crystal medium according to Claim 8 or 9, characterized in that the energy transfer agent comprises at least one compound having a unit of formula

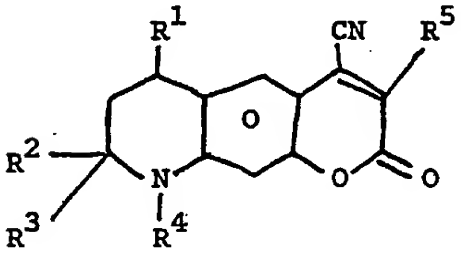
$$-Ar^1-Ar^2-Ar^3-$$

wherein Ar^1, Ar^2 and Ar^3 are identical or different and are selectred from the group consisting of unsubstituted 1,4-phenylen, 1,4-phenylen substituted by 1 or 2 fluorine atoms, and heteroaromatic ring structures.

11. Liquid crystal medium according to Claim 10 characterized in that the energy transfer agent comprises at least one anisotropic compound.

12. Liquid crystal medium according to one of Claims 8 to 11 characterized in that it comprises a mixed dye system.

13. Liquid crystal medium according to one of Claims 8 to 12 characterized in that it comprises a fluorescent dye of the general formula I

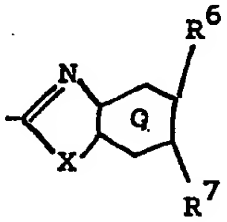
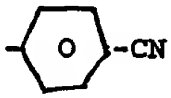


I

wherein

R^1, R^2 and R^3 are each independently alkyl with 1 to 6 carbon atoms

R^4 is alkyl or cycloalkyl with up to 7 carbon atoms possibly substituted once or twice with hydroxy, cyano, alkoxy with 1 to 3 carbon atoms or alkoxycarbonyl with 1 to 3 carbon atoms

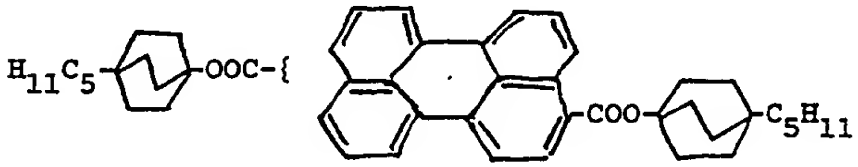
R^5 is  or 

R^6 and R^7 is hydrogen, chlorine, bromine, cyano, alkyl, alkoxy, alkoxycarbonyl or carbalkoxy each with up to 7 carbon atoms in the alkyl chain

X is O or N-R^8

R^8 is hydrogen or alkyl with 1 to 3 carbon atoms.

14. Liquid crystal medium according to Claim 12, characterized in that it comprises a green fluorescent dye of formula II

 II

and a red fluorescent dye.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 89/00932

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 09 K 19/60, G 02 F 1/13

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]:	C 09 K

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	WO, A, 87/05617 (GENERAL ELECTRIC) 24 September 1987, see page 2, lines 14-32; page 3, lines 5-16, 33-37; page 4, lines 1-5; example 2; claims 1,2,5, 6,7-9 --	1-4,8-11,14
Y	Proceedings Eurodisplay, 1987, M.R. Lewis et al.: "A fluorescent dyed-phase change liquid crystal display",pages 149-151, see page 149 (cited in the application) --	1-4,8-11, 14
Y	DE, A, 2837218 (SHARP) 8 March 1979, see claims 1-4,8; page 14, lines 9-16; page 15, lines 14-16; page 19, lines 5-21 & US, A, 4556287 (cited in the application) --	1,2,7,8,9, 14

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* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
29th September 1989	27 OCT 1989
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	T.K. WILLIS

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 4208106 (C. OH) 17 June 1980, see column 2, lines 47-50; column 3, lines 44-60; column 4, lines 61-68; column 5, lines 1-17; claims 1-4 (cited in the application)	1,7,8,14

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 8900932 SA 30324

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 18/10/89
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A- 8705617	24-09-87	EP-A,B	0261165	30-03-88
		GB-A-	2189502	28-10-87
		JP-T-	63503073	10-11-88
		US-A-	4838659	13-06-89
DE-A- 2837218	08-03-79	JP-A-	54151580	28-11-79
		JP-A-	55003466	11-01-80
		JP-A-	54048690	17-04-79
		CH-A-	636637	15-06-83
		US-A-	4337999	06-07-82
		CH-A,B	637261	29-07-83
		DE-A-	2837257	22-03-79
		US-A-	4556287	03-12-85
US-A- 4208106	17-06-80	None		